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On the Reversible Displacement
Of Mercury and Silver
In Aqueous Solutions

Chemical Engineering

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ON THE REVERSIBLE DISPLACEMENT OF MERCURY AND SILVER IN AQUEOUS SOLUTIONS: A STUDY OF THE REACTION $Hg + 2KAg(CN)_2 \rightleftarrows 2Ag + K_2Hg(CN)_4$.

BY

FRED STERLING LODGE

THESIS

For the Degree of Bachelor of Science

in Chemical Engineering

College of Science

University of Illinois

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

FRED STERLING LODGE

ENTITLED ON THE REVERSIBLE DISPLACEMENT OF MERCURY AND SILVER IN AQUEOUS SOLUTIONS: A STUDY OF THE REACTION $Hg+2KAg(CN)_2 = 2Ag+K_2Hg(CN)_4$

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Chemical Engineering

G. McP. Smith
Instructor in Charge.

APPROVED: W. A. Noyes.

HEAD OF DEPARTMENT OF Chemistry

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ON THE REVERSIBLE DISPLACEMENT OF MERCURY AND SILVER IN AQUEOUS SOLUTIONS: A STUDY OF THE REACTION $Hg + 2KAg(CN)_2 \rightleftarrows 2\ Ag + K_2Hg(CN)_4$.

The phenomena of displacement may be explained according to Nernst's theory of ionic electromotive activity, as follows:

When a metal is immersed in an electrolyte, free from ions of that metal, the solution pressure of the metal tends to drive particles of it into the solution. These particles or ions carry positive charges of electricity, from which it results that the solution becomes positively charged, and the metal negatively charged. These charges give rise to a force component, which, on the one hand, tends to prevent the entrance of more metallic ions in the solution, and, on the other hand, seeks to drive positive ions from the solution back to the metal.

One of two things can now take place; either the solution pressure of the metal is exactly compensated by the electrostatic charges, in which case there results an equilibrium corresponding to the point at which the difference in potential between the solution and the metal,

$$E = \frac{RT}{n} \cdot \log_{n} \cdot \frac{P}{p} .$$

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In this equation RT is the gas constant, P the solution pressure of the metal, p the osmotic pressure of the ions, and n the valence of the metal.*

Or, if the solution pressure of the metal is sufficiently high, ions of it continue to be driven into the solution, and the electrostatic charge becomes so great that ~~the~~ other positive ions in the solution are forced in the opposite direction from the solution to the metal; there they give up their charges and separate in the free state. This is the process which takes place, for example, when copper is precipitated from its salt solutions by zinc, or when water is decomposed by sodium.

In order that the second process may take place, the relation

$$\sqrt[n_1]{\frac{P_1}{p_1}} > \sqrt[n_2]{\frac{P_2}{p_2}}$$

must hold, in which the index I refers to the displacing metal and 2 to the metal displaced. P_1 and P_2 are the solution pressures of the metals, and p_1 and p_2 the osmotic pressures of respective ions in the solution.*

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*Since E = 0, when P = p, we see that the electrolytic solution pressure of a metal is a constant, equal in value to the osmotic pressure of its ions in a solution (free from other positive ions), with which it does not show any difference in potential.

*In words, the conditions favorable for the precipitation of the second metal are (1), Low solution pressure of the second metal and high osmotic pressure(i.e. high concentration) of its ions, and (2), high solution pressure of the

first metal, and low osmotic counter-pressure (low concentration) of its ions in the solution.

As a necessary consequence of this, it follows, that of any two metals, either can be made to displace the other from a solution, provided that the relative magnitudes of

$$\sqrt[n_1]{\frac{P_1}{p_1}} \quad \text{and} \quad \sqrt[n_2]{\frac{P_2}{p_2}}$$

can be reversed under different conditions.[*]

Previous Work.

Taking into consideration the fact that the osmotic pressure of metals, dissolved in mercury,[*] is proportional to their concentration in the mercury, A. Ogg[**] investigated the reversible reaction:

$$2Ag + Hg_2(NO_3)_2 \rightleftarrows 2AgNO_3 + 2Hg,$$

$$\text{or} \quad 2Ag + Hg_2^{\cdot\cdot} \rightleftarrows 2Ag^{\cdot} + 2Hg$$

He found that equilibrium was practically approachable from one side only (from right to left above) but that upon its attainment, the concentrations were such as to sat-

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[*] The value of P for a given metal may be raised by increasing the temperature, or lowered by alloying the metal with a second metal; the value of p may be raised by increasing the concentration, or lowered by dilution, or by combination of the ions in question with others to form an only slightly dissociated complex ion.

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[*] G. Meyer, Z. physik. Chem. 7, 477 (1891)

[**] A. Ogg, Ibid. 22; 536, (1897) ; 27; 285 (1898)

isfy the condition:

$$\frac{P_{Ag}}{p_{Ag}} = \sqrt[2]{\frac{P_{Hg}}{p_{Hg}}}$$

Since it was found that the value of n for mercury is 2, it follows that the metal exists in mercurous nitrate as a divalent ion, $Hg^{\cdot} - Hg^{\cdot}$, from which the correct formula for that salt is seen to be $Hg_2(NO_3)_2$

In a paper on the chemistry of the process of intensifying photographic negatives by the displacement from $HgCl_2$ solution of metallic mercury upon the silver image, Chapman Jones[*] contends that the white substance formed is a compound of the formula $AgHgCl_2$, and not a mere mixture of silver chloride and calomel. On treating the substance with 5 per cent KCN solution in excess, Jones says the primary reaction is

$$3AgHgCl_2 + 8KCN = Ag + Hg + 2KAg(CN)_2 + 2Hg(CN)_2 + 6KCl$$ [*]

He found, however, on analysis, that less silver and more mercury was present in the free state than corresponds to the equation; he explains the discrepancy by showing that mercury is precipitated from a solution of $Hg(CN)_2$ in the presence of KCN (i.e., from $K_2Hg(CN)_4$ solution), by metallic silver. He claims, on the other hand, that mercury does not precipitate silver from a solution of AgCl in KCN,(i.e.,

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[*] Jour. Soc. Chem. Ind. <u>12</u>; 983,(1903)

[*] The equation should be: $3AgHgCl_2 + 12\ KCN = Ag + Hg + 2KAg(CN)_2 + 2K_2Hg(CN)_4 + 6KCl$.

from a solution of $KAg(CN)_2$ in the presence of KCl.

Finally, the reversivle displacement of mercury and silver was studied in a preliminary paper by G. McP. Smith.* Among other reactions, that between metallic silver and $K_2Hg(CN)_4$ was investigated. It was found that the reaction is reversible and that a pasty amalgam can be obtained by starting either with metallic silver and $K_2Hg(CN)_4$ solution, or with metallic mercury and $KAg(CN)_2$ solution. It is with this reaction that the present investigation is concerned.

Experimental Part.

1. Preparation of the Silver. The silver was prepared and purified as follows:

575 grams of $FeSO_4$ were dissolved in 1500 cc. of water, the solution acidified with 5 cc. H_2SO_4 and filtered. A solution of 170 grams of $AgNO_3$ was added slowly, with constant stirring. The mixture was then warmed on a water bath for twelve hours to insure complete precipitation. The silver was filtered off into a Büchner funnel and washed repeatedly with portions of dilute hydrochloric acid, followed by repeated washings with hot distilled water, then with ammonia, then again with hot distilled

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*Jour. Amer. Chem. Soc. 27; 547 (1905)

water. The finely divided silver was then dried in an oven at 150 degrees.

2. Purification of the mercury. This metal was purified by shaking it with a dilute solution of $K_2Cr_2O_7$, to which a little sulphuric acid was added, washing with dilute nitric acid, and finally allowing the metal to fall in finely divided drops, several times in succession, from the end of a capillary funnel tube, through a long, upright vessel filled with a strong solution of mercuric nitrate, acidified with nitric acid. The purity was finally confirmed by analysis.

3. Preparation of the potassium silver cyanide. This salt was prepared from silver nitrate and potassium cyanide according to the following reactions:

$$AgNO_3 + KCN = AgCN + KNO_3$$

$$AgCN + KCN = KAg(CN)_2$$

100 grams of silver nitrate were dissolved in water and made up to 250 cc. To 125 cc. of this solution was slowly added a solution of 40 grams of potassium cyanide in 100 cc. of water, till the precipitate just dissolved. The solution was then filtered and the remaining 125 cc. of the silver nitrate solution added with constant stirring. The silver cyanide was precipitated according to the following quantitative reaction,

$$KAg(CN)_2 + AgNO_3 = 2AgCN + KNO_3$$

The precipitate of silver cyanide was washed four times by decantation, then on a Büchner funnel, using three liters of water in small portions and allowing complete drainage by

suction after each addition. The precipitate, after drying in a vacuum dessicator, weighed 136.5 grams. This precipitate was dissolved in a solution of potassium cyanide, using just enough to bring all the silver cyanide into solution. The solution was allowed to slowly evaporate in a crystallizing dish. The crystals were separated from the mother-liquor, dried by suction on a Büchner funnel, washed with a small quantity of distilled water and finally dried in an oven at 120 degrees.

4. <u>Preparation of the potassium mercury cyanide.</u> This salt was prepared from mercuric cyanide and potassium cyanide, according to the following reaction:

$$Hg(CN)_2 + 2KCN = K_2Hg(CN)_4.$$

A solution containing the two salts in the above molecular ratio was allowed to stand in a shallow crystallizing dish. Crystals of the complex salt $K_2Hg(CN)_4$ separated out. These crystals were separated from the mother-liquor, dried by suction and washed with a small amount of distilled water. They were then dried in an oven at 120 degrees.

5. <u>Quantitative proof of the reaction:</u>

$$2Ag + K_2Hg(CN)_4 = 2KAg(CN)_2.$$

To a solution of 10.0225 grams $K_2Hg(CN)_4$ in 25 cc. water, 5 grams of pure precipitated silver were added and the mixture was heated for two hours on a steam bath. The silver quickly darkened in color, caked up, and globules of an amalgam became visible. The solution was then separated quantitatively from the metallic residue, diluted to 100 cc. in a measuring

flask, and duplicate analyses made of 10 cc portions of the solution.

Analysis.

	A.	B.
AgCN	0.4291 gm.	0.4230 gm.
HgS	0.2368 "	0.2363 "

That is, the entire solution contained:

4.260 gm. AgCN $\Leftrightarrow$ 6.0807 gm. $K_2Hg(CN)_4$
2.365 " HgS $\Leftrightarrow$ 4.5225 " "
10.6032 " "
Instead of 10.0225 " "

The results here given are the best obtained in three series of experiments and, in view of the results obtained in the following experiments, it would appear that the analytical method is accurate enough. The discrepancy in the present case needs further investigation.

6. Quantitative proof of the reaction:

$$Hg + 2KAg(CN)_2 = K_2Hg(CN)_4 + 2Ag$$

I. 1 cc. of mercury was treated for one hour at 25 degrees with 15 cc. $KAg(CN)_2$ solution, measured from a burette. 5 cc. of the solution were taken for analysis.

On analysis, the solution gave (in 15 cc):

AgCN = 3 x 0.0456 gm. $\Leftrightarrow$ 0.2033 gm. $KAg(CN)_2$
HgS = 3 x 0.0830 " $\Leftrightarrow$ 0.4272 " "
0.6305 " "
Instead of 0.5975 " "

II. The above experiment was repeated, but the action was allowed to continue for three hours. 5 cc. of the solution

were taken for analysis.

On analysis the solution gave (in 15 cc.):

$AgCN = 3 \times 0.0431$ gm. $\asymp$ 0.1922 gm. $KAg(CN)_2$

$HgS = 3 \times 0.0808$ " $\asymp$ 0.4159 " "

0.6081 " "

Instead of 0.5975 " "

Since the results are practically the same after three hours as after one hour, it would appear that equilibrium was attained in less time than one hour.

III. To a solution of 10.0344 grams $KAg(CN)_2$ in 25 cc. of water, 25 grams of mercury were added and the mixture was heated for two hours on a steam bath. Crystals of solid amalgam separated at the surface of the mercury. The solution was then separated from the metallic residue and diluted to 100 cc. in a measuring flask. Duplicate analyses were made of 10 cc. portions of the liquid. The amalgam was also dissolved in nitric acid and the excess of acid largely removed by evaporation. The residue was dissolved, made up to 250 cc. in a measuring flask and two 10 cc. portions of the liquid analyzed for silver.

Analyses.

10 cc. solution gave:	A.	B.
$AgCN$	0.3597 gm.	0.3599 gm
HgS	0.2730 "	0.2725 "
1/25 of the amalgam gave:		
$AgCl$	0.1349 "	0.1343 "

That is, the entire solution contained:

$AgCN$ = 3.5980 gm. $\Bumpeq$ 5.3490 gm. $KAg(CN)_2$
HgS = 2.7280 " $\Bumpeq$ 4.6804 " "
10.0294 " "
Instead of 10.0344 " "

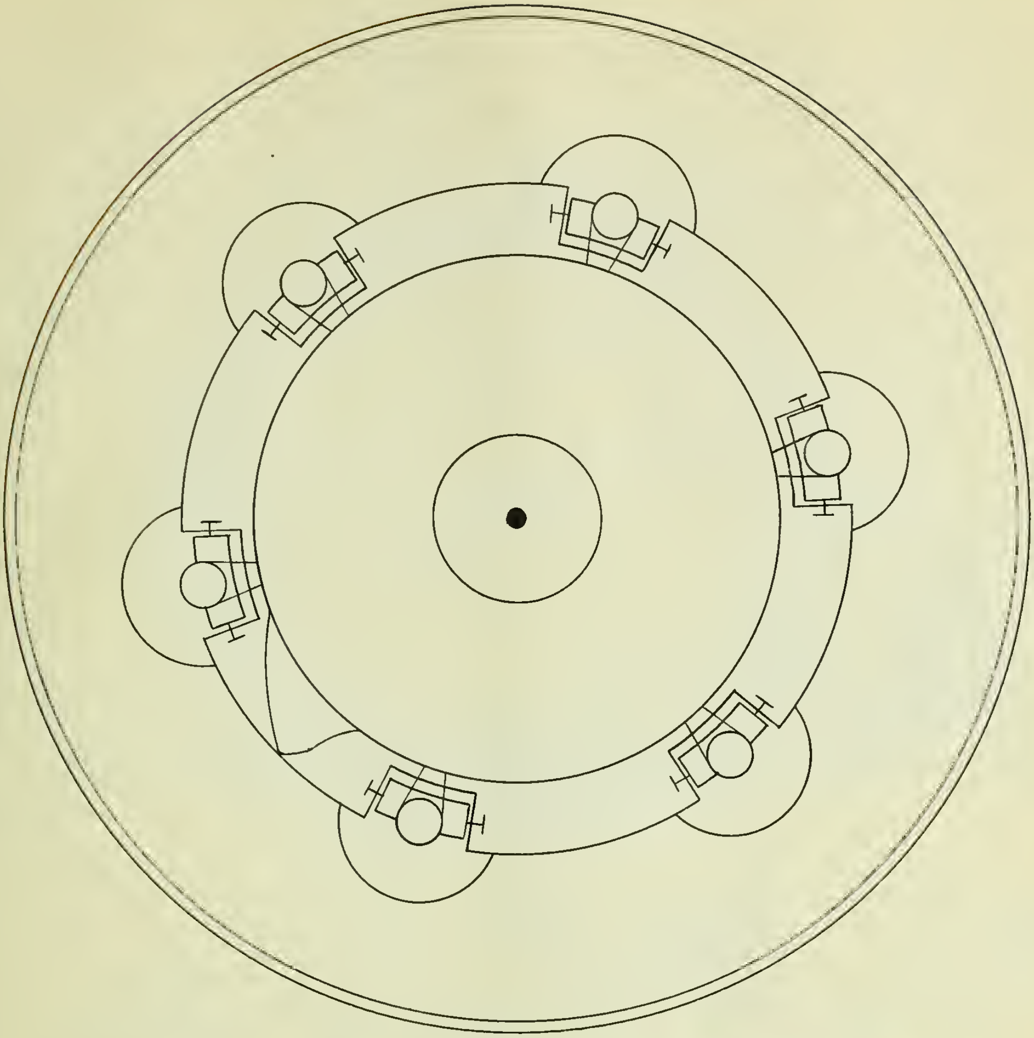
The total amalgam gave:

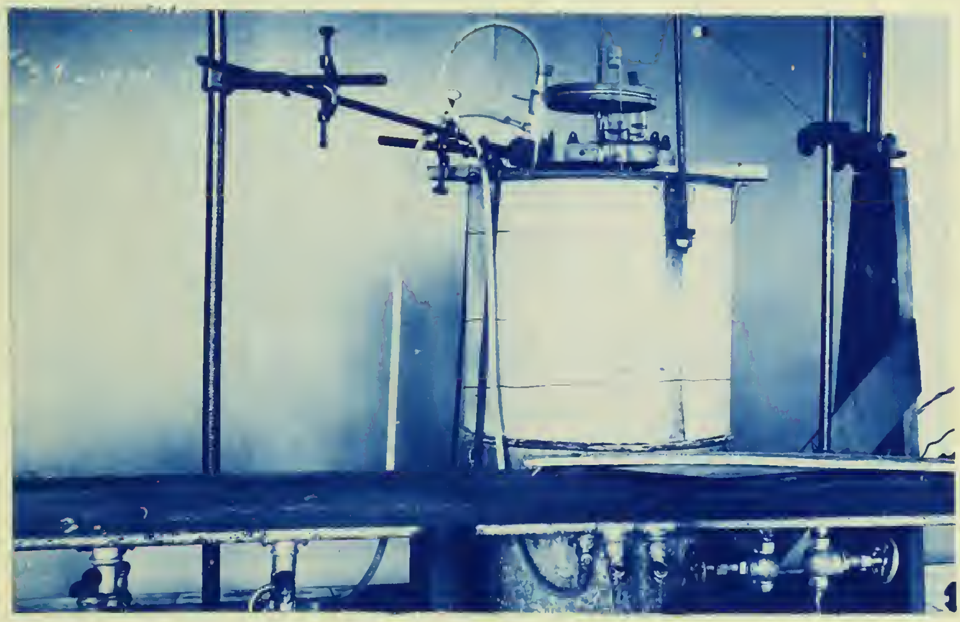
$AgCl$ = 3.3650 gm. $\Bumpeq$ 4.6739 gm. $KAg(CN)_2$
(2.7280 gm. HgS $\Bumpeq$ 4.6804 " ")

The results of the three foregoing series of experiments prove conclusively that mercury precipitates silver from the complex cyanide solution, in accordance with the equation

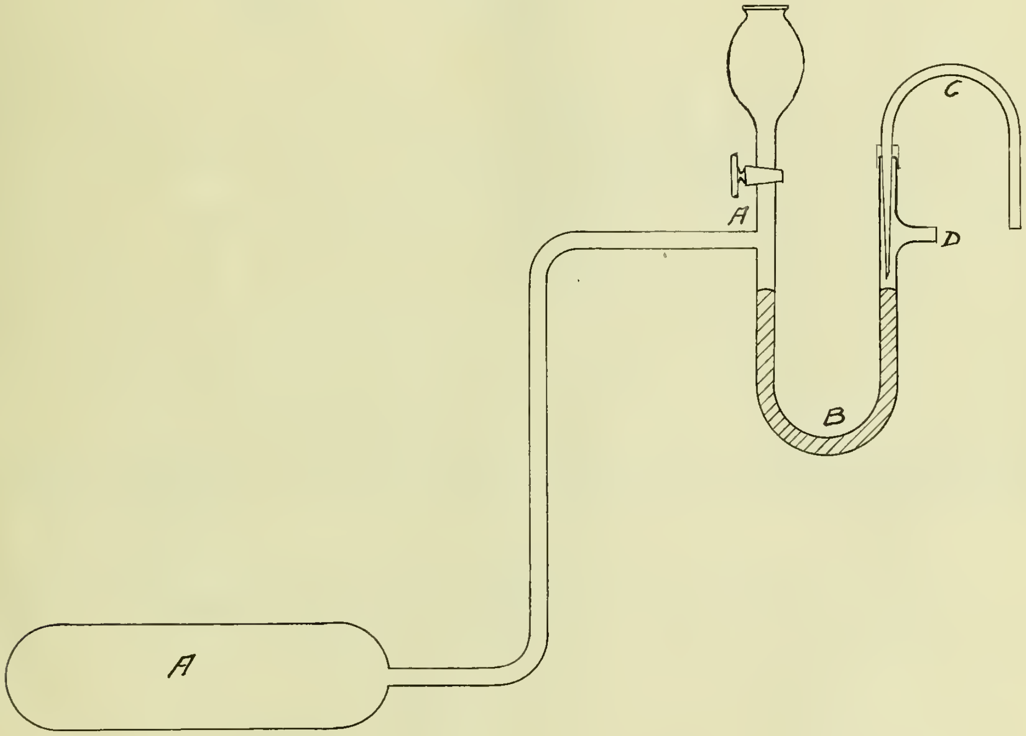
$$Hg + 2KAg(CN)_2 = K_2Hg(CN)_4 + 2Ag$$

7. Description of the thermostat and shaking machine for the equilibrium experiments. For carrying out the equilibrium experiments, a machine was designed as shown by the accompanying sketches and pictures. The machine consisted essentially of a sheet iron thermostat vessel, twelve inches in diameter and twelve inches in depth. In the center was fixed a shaft bearing a fan on the lower end for keeping the water properly agitated. On the top end of the shaft was a pulley driven by a belt from a reducing shaft connected to an electric motor. Three inches above the water level of the thermostat was a notched disc, as shown in the sketch. This disc was supported from the sides of the vessel and, in turn, supported the bottles to be shaken. These bottles were long necked, melting point flasks of 100 cc. Capacity, and were held four inches from the top by elastics in wooden collars kept in the notches by steel pinions. These pinions were held in position by curtain fixtures, thus allowing free





motion in a radial direction to the thermostat. Elastics from the necks to the disc held the bottles with the necks in toward the center shaft. Three inches above the supporting disc, was another fastened to the revolving center shaft. This disc bore a wire cam, which, upon revolving struck the necks of the bottles, forced them out, to be returned by the elastic when the cam had passed. This caused a thorough shaking of each bottle, every revolution of the fan stirrer. This arrangement allowed the bulb of the flask to be entirely submerged in the water of the thermostat. The thermostat was kept constant to within one-tenth of a degree by a micro-burner connected to a regulator as shown in the sketch.



The bulbs and tubes A,A are filled with toluene, and B, with mercury. C is drawn out into a capillary with a diagonal opening. Expansion of the toluene forces the mercury up, thus cutting off some of the gas supply entering through C, and reducing the flame in the micro-burner at the end of D.

Equilibrium Experiments.

Since, in the reversible reaction,

$$Hg + 2KAg(CN)_2 \rightleftarrows 2Ag + K_2Hg(CN)_4$$

the mercury and silver displace one another in equivalent quantities, the reaction will proceed in one or the other direction until the point is reached at which

$$\sqrt[2]{\frac{P_{Hg}}{p_{Hg}}} = \frac{P_{Ag}}{p_{Ag}}$$

when equilibrium will be attained. By acting upon mercury in such excess that its active mass may be considered as constant, with a solution containing both $KAg(CN)_2$ and $K_2Hg(CN)_4$ and of such concentration that (1) no solid amalgam separates*; or (2) solid amalgam does separate in every case, we should expect to obtain in the first case the relation

$$\frac{a}{c\sqrt{b}} = K$$

or, in the second case, the relation,

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*At the ordinary temperature, 100 grams of saturated liquid silver amalgam contains 0.03 grams Ag. (Goüy. J. de Phys. 4; 320 (1895)

$$\frac{a}{\sqrt{b}} = K,$$

where a and b are the concentrations of the Ag and Hg ions in the solution and c the concentration of the Ag in the liquid amalgam. Assuming the concentration of Ag and of Hg to be proportional to that of $KAg(CN)_2$, and of $K_2Hg(CN)_4$, respectively, we may use these values directly, instead of a and b in the above expressions.* Starting with definite volumes of solutions containing known quantities of $KAg(CN)_2$ and $K_2Hg(CN)_4$, and with a large excess of mercury, the values of a, b, and c at equilibrium can all be obtained by simply determining the $KAg(CN)_2$ then in the solution as AgCN, by precipitation with dilute hydrochloric acid. From the difference between this amount and that present at the start, we have only to calculate the equivalent amount of $K_2Hg(CN)_4$ and add it to the amount originally present. The silver displaced is, of course, in the amalgam. That this method is practical is shown by the following trial analyses.

50 cc of the solution were known to contain:

$KAg(CN)_2$ = 1.5199 gm.

$K_2Hg(CN)_4$= 0.7084 ".

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*Working under the same conditions with $Hg_2(NO_3)_2$ and $AgNO_3$ and a large excess of mercury, Ogg(loc.cit.) showed that

$$\frac{a}{c\sqrt{b}} = K$$

in the first case and that

$$\frac{a}{\sqrt{b}} = K$$

in the second case.

Silver determinations were made with 20 cc. samples of the liquid with the following results:

AgCN = A. 0.4141 gm.
= B. 0.4123 "
mean 0.4132 "

Theoretical value:

AgCN = 0.4091 gm.

The error does not amount to more than 1 per cent.

8. <u>Time necessary for the attainment of equilibrium</u>. In the investigation already cited, Ogg treated an excess of mercury (in portions of 1 cc.) with solutions containing $Hg_2(NO_3)_2$ and $AgNO_3$ in varying but known amounts, and found that the reaction is very rapid; equilibrium resulted in all cases within one-half hour. On treating pure, finely divided silver with the same solutions, however, the precipitated mercury appeared to amalgamate only on the surface of the silver, and equilibrium was not attained.

In the present instance it was sought to ascertain the time necessary for equilibrium by shaking mercury in portions of 1 cc. with 15 cc. of a solution made by mixing 15 cc. $N/5KAg(CN)_2$, 15 cc. $N/5K_2Hg(CN)_4$ and 20 cc. of water. The tests were performed simultaneously in the thermostat at 25 degrees to 25.1 degrees. At intervals duplicate portions of 20 cc. of solution were withdrawn from one of the four flasks and analyzed for silver. The mixture in the first flask was allowed to act one-half hour and those in the other flasks were allowed to act one hour, one and one-half hour,

and one and three-quarters of an hour respectively. The results are given below:

At the start 20 cc. of solution contained $KAg(CN)_2$ equivalent to 0.1608 gr AgCN, provided there was no change in volume upon mixing.

Time	1/2 hour	1 hour	1-1/2 hour	1-3/4 hour
AgCN from 20 cc.	0.1621 g.	0.1614g.	0.1591 g.	0.1574 g.

From these results, it would appear that the reaction was very slow, since there was practically no change in one hour and three-quarters. This, however, is almost certainly not the case, and it is possible that in this series of experiments, the relative concentration of Hg ions in the solution was greater than that which would obtain at equilibrium. In that case, the reaction could not proceed in the absence of metallic silver. The first of these conclusions is supported by the results obtained in No. 6,(Experiments 1 and 2), in which an excess of mercury was treated with N/5 $KAg(CN)_2$ solution. In that case equilibrium was attained in less than one hour, as is shown by the fact that at the end of that time the solution gave 0.1368 g. AgCN, the same quantity that was found in a duplicate experiment at the end of three hours (0.1293g.) But, at equilibrium (Experiments 1 and 2) the concentration of the $KAgCy_2$ was approximately 0.07 normal as compared with 0.13 normal for the K_2HgCy_4; while,in the present series of experiments, both concentrations remained fairly constant for one hour and three-quarters, at 0.06 normal. If, then, the second conclusion drawn above

is correct, and the concentration of Hg ions was too great in this series, it follows that the actual ionic concentration of Hg is greater in 0.062 normal solution of $K_2Hg(CN)_4$ than is the case in a 0.13 normal solution; in other words, that the complexanion $Hg(CN)_4''$ is increasinly dissociated on dilution with water, according to the equation:

$$Hg(CN)_4'' \rightleftarrows Hg^{\cdot\cdot} + 4CN'$$

Owing to lack of time these questions could not at present be further investigated.

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